

PCTWORLD INTELLECT
Int

WO 9604427A1

INTERNATIONAL APPLICATION PUBLISHED

(51) International Patent Classification 6 : E01C 19/10, C08L 95/00		A1	(11) International Publication Number: WO 96/04427
			(43) International Publication Date: 15 February 1996 (15.02.96)
(21) International Application Number: PCT/EP95/02819		(81) Designated States: NO, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).	
(22) International Filing Date: 18 July 1995 (18.07.95)		Published <i>With international search report.</i>	
(30) Priority Data: 94/09461 29 July 1994 (29.07.94) FR			
(71) Applicant: ESSO SOCIETE ANONYME FRANÇAISE [FR/FR]; 2, rue de Martinets, F-92569 Rueil-Malmaison Cédex (FR).			
(72) Inventor: BOUSSAD, Nadjib ; Esso Société Anonyme Française, Centre de Recherches, Boîte postale 6, F-76130 Mont-Saint-Aignan (FR).			
(74) Agent: SOMERS, Harold, Arnold ; Esso Engineering (Europe) Limited, Patents and Licences, Mailpoint 72, Esso House, Ermyrn Way, Leatherhead, Surrey KT22 8XE (GB).			
(54) Title: PROCESSES FOR THE PREPARATION OF BITUMINOUS COLD-MIX			
(57) Abstract <p>A bituminous cold-mix for road building and similar paving uses is made by a process comprising the steps of: (a) applying to an aggregate of mixed particle size a first bitumen emulsion of relatively high breaking index (e.g., 190 or more, NFT 66.017) to coat at least 80 % of the aggregate surface with no more than 5 weight % (e.g. about 2 weight %) of residual bitumen; and (b) applying to the coated aggregate from step (a) a second bitumen emulsion having a breaking point no higher (e.g., 190 or less) than that of the first emulsion to produce fully coated aggregate particles. The invention also includes roadways and similar paved areas constructed using the cold- mix.</p>			

BEST AVAILABLE COPY

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

**PROCESS FOR THE PREPARATION OF
BITUMINOUS COLD-MIX**

The present invention relates to the preparation of bituminous cold-mix, principally for the surfacing of roads.

Cold bitumen emulsions provide a useful alternative to molten bitumen for coating aggregate for application as cold-mixes to roads and similar surfaces subjected to traffic or other hard wear. Cold mixes have the advantage that they can be applied at low temperatures, e.g. at locations where heating equipment is not readily available. After the cold-mix is applied to the road surface, the emulsion breaks and bitumen deposits on and coats the aggregate particles.

There are, however, a number of problems associated with cold-mixes.

To obtain the best performance, it is desirable to use a hard bitumen. However, hard bitumens, e.g. having a penetration (pen value) of 80 or below (according to NFT 66.004, where NFT designates the French standard Normale Française Technique, or ASTM D5-86), are brittle and deficient in tack, which leads to a low compaction efficiency. Solvents are often added, resulting in a fluxed bitumen, to lower the viscosity of the bitumen at emulsification temperature and make the application of the cold-mix easier. However the use of solvents has the drawback that they require time to evaporate.

Road surfaces are designed by testing core samples in modulus and fatigue. When hot-coated aggregate is applied it is possible to take core samples a few days afterwards. With samples of surface laid using emulsion, the cores tend to break up if taken within several months after laying. Early coring problems are due to slow build-up of cohesion and this in turn can be caused by inefficient coating of the aggregate and

high void content in the structure. Aggregate is constituted of a mixture of particles of different sizes, from fine powder and sand up to e.g. 35 mm. The finer particles in the aggregate spectrum are easier to coat than the larger particles. Attempts have been made to reduce this problem by successively coating larger and smaller fractions, as described in EP-A-524031. However, early coring remains problematic.

The invention is aimed at providing a process for the preparation of bituminous cold-mix which permits the use of hard bitumen while achieving a rapid cohesion build-up and acceptably early coring.

The present invention provides a process for preparing a bituminous cold-mix for road building and similar paving uses, comprising the steps of :

- (a) applying to an aggregate of mixed particle size a first bitumen emulsion of relatively high breaking index (e.g., 190 or more, NFT 66.017) to coat at least 80% of the aggregate surface with no more than 5 weight % of residual bitumen; and
- (b) applying to the coated aggregate from step (a) a second bitumen emulsion having a breaking point no higher (e.g., 190 or less) than that of the first emulsion to produce fully coated aggregate particles.

Preferably step (a) provides the said coating with no more than 2.5 wt.% residual bitumen.

Preferably, the bitumens of the first and second emulsions each have a softening point (NFT 66.008) in the range of from 20 to 85 and a penetration (pen value) (NFT 66.004) in the range of from 20 to 400, e.g. from 20 to 80. Preferably, the bitumen of the first emulsion has a pen value in the range of from 20 to 80 (e.g., from 35 to 55, and usually from 40 to 50). The bitumen of the second emulsion may have a pen value equal to or greater than that of the bitumen of the first emulsion.

The bitumen of the second emulsion may be a polymer-modified bitumen. The polymer may have a number average molecular weight (M_n) in the range of from 2000 to 300,000. The bitumen may be modified with up to 10 wt.% of polymer (homopolymer or copolymer). Examples of suitable polymers are styrene/butadiene/styrene (SBS), ethene/vinyl acetate copolymer (EVA) and polyethylmethacrylate (EMA). The polymers may have a number average molecular weight (M_n) in the range of from 2,000 to 300,000 (as determined by gas phase chromatography : GPC).

The bitumen of the second emulsion may be fluxed. The use of fluxed bitumen provides the advantage of good storage stability, but is attended with the disadvantages already mentioned.

From 1 to 4 wt.% (e.g., from 1 to 3 wt.%) (based on the weight of coated aggregate) of the first emulsion may be used in step (a) and/or from 3 to 7 wt.% (e.g., from 3 to 6 wt.%), based on the weight of coated aggregate, of the second emulsion may be used in step (b).

At least the first emulsion may have a particle diameter in the range of from 2 to 8 μm (e.g., 2 to 6 μm) with a standard deviation of less than 0.3 (e.g., no more than 0.25).

At least the first emulsion may be prepared using a static mixer or a plurality of serially-connected static mixers.

The invention also provides a road or similar paved area constructed using a bituminous cold-mix composition made by the process as herein described.

The first emulsion can be considered to be over-stabilised. This is desirable in order to ensure that it can be kept in storage and re-coated at a later stage. It also helps to ensure a fine emulsion and efficient coating. The stability of emulsions can be measured by the LCPC French standard Laboratoire Centrale des Ponts et Chemins breaking index (NFT 66.017) and is normally controlled through the proportion of

- 4 -

emulsifier used. A larger amount of emulsifier may be used in the first emulsion than in the second. The proportion of emulsifier in the first emulsion is preferably selected to produce a breaking index of 190 or above.

On the other hand, the proportion of emulsifier in the second emulsion is preferably selected to produce a breaking index no higher than 190.

For reasons of logistics, the first emulsion and the second emulsion may be substantially identical, thereby avoiding the necessity to manufacture and store two types of emulsion. On the other hand, there might be situations wherein there is considered to be no drawback in utilizing a high breaking index first emulsion and a lower breaking index second emulsion.

The content of emulsifier in said first emulsion may be from 0.8 to 2 wt.% and the content of emulsifier in said second emulsion may be from 0.1 to 0.8 wt.%, based on the total weight of emulsion. However, as already indicated, the amounts of emulsifier in both emulsions may be about the same for logistical reasons.

Cationic emulsifiers are preferred, especially compounds resulting from the reaction of an amine having 10 or more carbon atoms with an inorganic acid. Especially preferred are salts of tallow polyamine (more especially in the first emulsion) and tallow diamine.

Although the preferred second emulsions may be selected so as to be not very storage-stable, their breaking occurs after a controlled delay and this ensures a rapid cohesion build-up in the cold-mixes.

In order to achieve 100% coating of the final particles it is important that as complete a coverage of the aggregate is achieved in the first coating over the whole particle size spectrum. Coating should be at least 80% complete, more preferably 85% or 90% or more. In order to achieve this, it is advantageous for the emulsion to be in the form of very fine and substantially uniform particles. Thus preferably at least the first

emulsion has a median particle diameter from 2 to 8 μm , more preferably from 2 to 6 μm . Preferably the standard deviation in median particle diameter is less than 0.3, more preferably less than 0.25. In the preferred process to be described both emulsions are prepared in the same way. This may be accomplished for the first and preferably also the second emulsion utilising a static mixer or a plurality of serially-connected static mixers.

A particularly advantageous plural stage static mixing process is that described in the Applicant's European patent publication EP-A-283246. Thus the present preferred process comprises:

- (a) feeding the bitumen into a first static mixer at a temperature above 50°C,
- (b) introducing water under pressure into the first static mixer, the pressure being sufficient to prevent substantial vaporisation of the water,
- (c) introducing an emulsifier into the first static mixer,
- (d) mixing the bitumen, water and emulsifier in the first static mixer,
- (e) passing the resultant mixture from the first static mixer to a second static mixer in which the temperature is lower than that prevailing in the first static mixer and below the boiling point of water,
- (f) passing the mixture through the second static mixer, and
- (g) removing the bitumen emulsion product from the second static mixer without substantial loss of water.

The temperature in the first static mixer is preferably from 110°C to 150°C, and the pressure in the first static mixer is preferably from 2 to 80 bar.

In the preferred process the mixture passing through the second static mixer is subjected to a pressure drop and cooling whereby the product emerges at substantially atmospheric pressure and below 100°C.

Using emulsions prepared by the process of EP-A-283246, it is possible to obtain 90% coating of the particles with a maximum of 2.5 wt.%, e.g. 2 wt.% or less, residual bitumen.

From 1 to 4 wt.%, e.g. from 1 to 3 wt.% emulsion is preferably added to the aggregate in the first coating step and from 3 to 7 wt.%, e.g. from 3 to 6 wt.% in the second step (based on the weight of coated aggregate).

The bitumen used in the first emulsion may be a natural bitumen resulting from the distillation of crude oil. This may also be used in the second emulsion, although the latter may also be a modified or fluxed bitumen.

The process of the invention leads to high performance cold-mixes which are readily cored and have the appearance of hot-mix material. The following examples further illustrate the invention.

In the following examples two Kenics® static mixers as described in Chemineers Brochure 800E published in 1984 by Chemineer Ltd. were used in series with the outlet of the first mixer leading directly to the inlet of a larger diameter mixer, as described in EP-A-283246. Bitumen at 130°C to 170°C was pumped into the first mixer. Water and emulsifier were introduced under pressure into the bitumen upstream of the inlet. The conditions in the first mixer were: temperature 110°-150°C and pressure 10 to 80 bar. The product from the first mixer was fed to the second mixer and quench dilution water was added at the inlet of the second mixer. The conditions in the second mixer were such that the product emerged at atmospheric pressure and at approximately 80° to 95°C. The amine emulsifier was in each case neutralised with sufficient hydrochloric acid to bring the final emulsion to a pH of from 2 to 4.5.

EXAMPLE 1

A first 60 wt.% emulsion was prepared (as above) from natural 40/50 pen bitumen using 1.3 wt.% (based on the weight of emulsion) of tallow polyamine chloride (CECA Polyram[®] S, obtainable from British Ceca Co. Ltd., London, U.K.) as emulsifier. The emulsion had the following characteristics:

Median particle diameter 3.8 μm (measured by Coulter[®] counter)

Standard deviation 0.16

Breaking index 250

A cold mix was prepared using 2.2 wt.% of this emulsion and 0/20 mm diorite aggregate. The aggregate was 100% coated and was found to be workable after one week of storage.

A second 60 wt.% emulsion was prepared similarly from 40/50 pen natural bitumen using 0.2 wt.% tallow diamine chloride as emulsifier. The characteristics of this emulsion are as follows:

Median particle diameter 4.0 μm

Standard deviation 0.16

Breaking index 120

A cold mix was prepared using 2.2 wt.% of this emulsion and the pre-coated 0/20 mm diorite aggregate from the first stage. Diorite aggregate is commonly used as a standard aggregate for this type of experiment. This material was 100% coated. It had the appearance of a hot mix and after compaction was found to be very cohesive.

EXAMPLE 2

A first 60 wt.% emulsion was prepared (as above) from natural 40/50 pen bitumen using 1.3 wt.% (based on the weight of emulsion) of tallow polyamine chloride

(as in Example 1) as emulsifier. A slightly lower pressure was used than in Example 1. The emulsion had the following characteristics:

Median particle diameter 5.1 μm

Standard deviation 0.22

Breaking index 239

A cold mix was prepared using 2.2 wt.% of this emulsion and 0/10 mm diorite aggregate. The aggregate was 100% coated and was found to be workable after two weeks of storage.

A second 60 wt.% emulsion was prepared similarly from 40/50 pen natural bitumen using 0.2 wt.% tallow polyamine chloride as emulsifier. The characteristics of this emulsion are as follows:

Median particle diameter 5.2 μm

Standard deviation 0.22

Breaking index 110

A cold mix was prepared using 6.0 wt.% of this emulsion and the pre-coated 0/10 mm diorite aggregate from the first stage. This material was 100% coated and had the appearance of a hot mix. A slab was manufactured and cored after three weeks of storage at ambient temperature. The dynamic moduli and fatigue behaviour were determined with the following results using the Esso Road Design Technology (ERDT) technique described in Celard, B., Proceedings of the 4th International Conference, Structural Design of Asphalt Pavements, Ann Arbor 1977, vol. 1, page 26.

Dynamic modulus (Mpa)		
Frequency (Hz)	10°C	20°C
20	5341	2893
10	4700	2407
3	3786	1691
1	2943	1215
0.3	2202	816
0.1	1645	570

The fatigue behaviour for the materials used in this example is described by the following equation:

$$\log_{10}(N) = [-2.985 \log_{10}(\epsilon_0)] - 7.724$$

at 10°C and 10 Hz.

In the equation, N is the number of cycles to failure, and ϵ_0 is the initial strain.

We believe this is the first occasion on which the fatigue behaviour of a cold mix has been determined in this way.

In this example, not only was the slab easily cored, but clear modulus measurements were possible.

EXAMPLE 3

The preparation of the pre-coated particles or (first stage cold-mix) repeated the procedure of Example 2.

A 65 wt.% emulsion was prepared similarly from a bitumen of 180/220 pen fluxed with 6 wt.% of kerosene, using 0.2 wt.% tallow polyamine hydrochloride as emulsifier.

A cold mix was prepared using 2.2 wt.% of this emulsion and the pre-coated aggregate from the first stage. The characteristics of this emulsion are as follows:

Median particle diameter 7.5 μm

Standard deviation 0.18

Breaking index 148

A complete coating was obtained and the resulting cold-mix was found to have excellent storing properties.

EXAMPLE 4

The preparation of the pre-coated particles or (first stage cold-mix) repeated the procedure of Example 2.

A 65 wt.% emulsion was prepared similarly from a natural 180/220 pen bitumen modified with 5 wt.% of SBS polymer of M_n about 200,000, using 0.2 wt.% tallow polyamine chloride (as in Example 1) as emulsifier.

A cold mix was prepared using 2.2 wt.% of this emulsion and the pre-coated 0/20 mm diorite aggregate from the first stage. A complete coating was obtained.

A slab was manufactured and cored after three weeks of storage at room temperature. The dynamic modulus was measured with the following results:

Dynamic modulus (Mpa)

Frequency (Hz)	10°C	20°C
20	2028	1032
10	1691	829
3	1559	542
1	548	285
0.3	303	80
0.1	162	21

The fatigue behaviour was also determined using the equation, for 10°C and 10 Hz :

$$\log_{10}(N) = [-2.911 \log_{10}(\epsilon_0)] - 6.648$$

wherein N and ϵ_0 have the meanings explained in Example 2.

The coefficients and constants in the equation relate to the materials used in Example 4. They differ from their Example 2 counterparts because the materials used in Example 2 are different.

CLAIMS:

1. A process for preparing a bituminous cold-mix for road building and similar paving uses, comprising the steps of:
 - (a) applying to an aggregate of mixed particle size a first bitumen emulsion of relatively high breaking index (e.g., 190 or more, NFT 66.017) to coat at least 80% of the aggregate surface with no more than 5 weight % of residual bitumen; and
 - (b) applying to the coated aggregate from step (a) a second bitumen emulsion having a breaking point no higher (e.g., 190 or less) than that of the first emulsion to produce fully coated aggregate particles.
2. The process of claim 1 wherein step (a) provides the said coating with no more than 2.5 wt.% residual bitumen.
3. The process of claim 1 or claim 2 wherein the bitumen of the first and second emulsions each has a softening point (NFT 66.008) in the range of from 20 to 85 and a penetration (pen value) (NFT 66.004) in the range of from 20 to 80.
4. The process of claim 3 wherein the bitumen of the first emulsion has a pen value in the range of from 20 to 80 (e.g., from 35 to 55).
5. The process of any one of claims 1 to 4 wherein the bitumen of the second emulsion has a pen value equal to or greater than that of the bitumen of the first emulsion.
6. The process of any one of claims 1 to 5 wherein the bitumen of the second emulsion is a polymer-modified bitumen, and wherein the polymer may have a number average molecular weight (M_n) in the range of from 2000 to 300,000.

7. The process of any one of claims 1 to 6 wherein the bitumen of the second emulsion is fluxed.
8. The process of any one of claims 1 to 7 wherein from 1 to 4 wt.% (e.g., from 1 to 3 wt.%) (based on the weight of coated aggregate) of the first emulsion is used in step (a) and/or from 3 to 7 wt.% (e.g., from 3 to 6 wt.%), based on the weight of coated aggregate, of the second emulsion is used in step (b).
9. The process of any one of claims 1 to 8 wherein at least the first emulsion has a particle diameter in the range of from 2 to 8 μm (e.g., 2 to 6 μm) with a standard deviation of less than 0.3 (e.g., no more than 0.25).
10. The process of any one of claims 1 to 9 wherein at least the first emulsion is prepared using a static mixer or a plurality of serially-connected static mixers.
11. A road or similar paved area constructed using a bituminous cold-mix composition made by the process of any one of claims 1 to 10.

INTERNATIONAL SEARCH REPORT

Inter national Application No
PCT/EP 95/02819

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 E01C19/10 C08L95/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 E01C C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP-A-0 589 740 (CECA) 30 March 1994 see the whole document ---	1, 11
A	EP-A-0 524 031 (COLAS) 20 January 1993 cited in the application see the whole document ---	1, 11
A	FR-A-2 623 219 (MAHEAS) 19 May 1989 see the whole document ---	1, 11
A	DE-A-19 41 688 (GOLDSCHMIDT) 18 February 1971 see page 7, line 14 - line 20; claims ---	1, 11
A	EP-A-0 283 246 (EXXON CHEN. PATENTS) 21 September 1988 cited in the application see the whole document -----	1, 9-11

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *B* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- *Z* document member of the same patent family

Date of the actual completion of the international search

31 October 1995

Date of mailing of the international search report

20. 11. 95

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+31-70) 340-3016

Authorized officer

Dijkstra, G

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter. Application No
PCT/EP 95/02819

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0589740	30-03-94	FR-A- 2695664	18-03-94
		CA-A- 2106018	15-03-94
		JP-A- 6207106	26-07-94
		NO-A- 933257	15-03-94

EP-A-0524031	20-01-93	FR-A- 2679274	22-01-93
		AT-T- 117390	15-02-95
		DE-D- 69201222	02-03-95
		DE-T- 69201222	29-06-95
		ES-T- 2066577	01-03-95

FR-A-2623219	19-05-89	EP-A, B 0384094	29-08-90
		US-A- 4978393	18-12-90

DE-A-1941688	18-02-71	NONE	

EP-A-0283246	21-09-88	AU-B- 600102	02-08-90
		AU-B- 1313988	15-09-88
		AU-B- 610138	16-05-91
		AU-B- 1314088	15-09-88
		AU-B- 7193491	30-05-91
		CA-A- 1331332	09-08-94
		DE-A- 3880182	19-05-93
		DE-D- 3886573	10-02-94
		DE-T- 3886573	28-04-94
		EP-A, B 0283247	21-09-88
		ES-T- 2047543	01-03-94
		JP-A- 1004238	09-01-89
		JP-A- 64000162	05-01-89
		KR-B- 9500039	07-01-95
		US-A- 4832747	23-05-89
		US-A- 5236624	17-08-93

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

☐ BLACK BORDERS

☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES

☐ FADED TEXT OR DRAWING

☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING

☐ SKEWED/SLANTED IMAGES

☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS

☐ GRAY SCALE DOCUMENTS

☒ LINES OR MARKS ON ORIGINAL DOCUMENT

☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY

☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.